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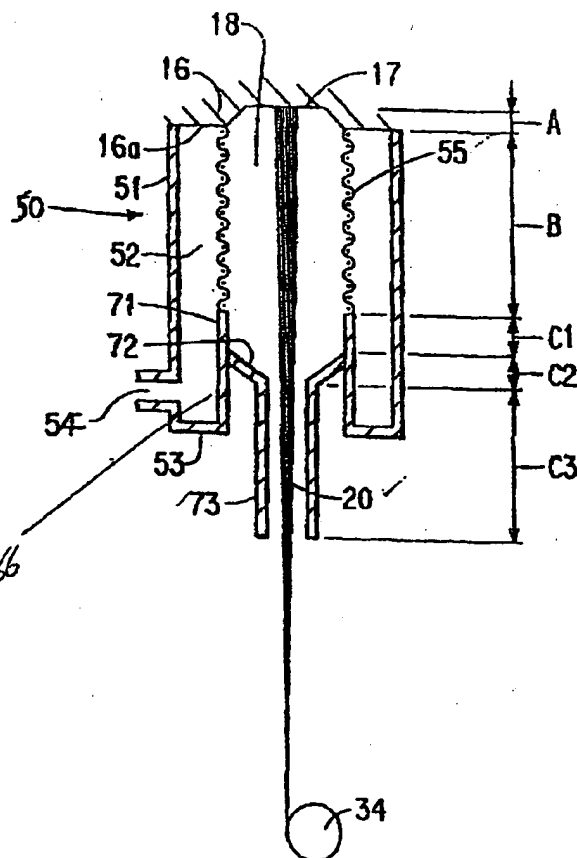
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(54) Title: METHOD OF PRODUCING POLYMERIC FILAMENTS



(57) Abstract: A method of making polymeric, e.g., polyester, filaments having low denier spread by use of a polymer of high viscosity is described. The filaments are useful to make yarns and other articles.

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TITLE OF INVENTION5 METHOD OF PRODUCING POLYMERIC FILAMENTSBACKGROUND OF THE INVENTION

1. Field of the Invention.

10 The present invention relates to methods for making polymeric filaments, such as polyester filaments, having low denier spread. The invention also relates to yarns and other articles formed from such filaments.

15

2. Description of Related Art.

 Many synthetic polymeric filaments, such as polyesters, are melt-spun, i.e., they are extruded from a heated polymeric melt. Melt-spun polymeric filaments
20 are produced by extruding a molten polymer, such as polyethylene terephthalate and related polyesters, through a spinneret with a plurality of capillaries, which can range in number, for example, from about 10 to about 300. The filaments exit the spinneret and are
25 then cooled in a cooling zone. The details of the cooling (quenching) and subsequent solidification of the molten polymer can have a significant effect on the quality of the spun filaments, as indicated by denier spread and inter-filament uniformity.

30 Methods of quenching include cross-flow, radial, and pneumatic quench. Cross-flow quenching involves blowing cooling gas transversely across and from one side of a freshly extruded filamentary array. Cross-flow quenching has generally been favored by many fiber
35 engineering firms as puller roll speeds (also known as "withdrawal speeds" and sometimes referred to as spinning speeds) have increased because of a belief that "cross-flow quench" provides the best way to blow

the larger amounts of cooling gas required by increased speeds or through-put.

Another type of quench is referred to as "radial quench" and has been used for commercial manufacture of some polymeric filaments, e.g., as disclosed by Knox in U.S. Pat. No. 4,156,071, and by Collins, et al. in U.S. Pat. Nos. 5,250,245 and 5,288,553. In this type of "radial quench" the cooling gas is directed inwards through a quench screen system that surrounds the freshly extruded filamentary array. Such cooling gas normally leaves the quenching system by passing down with the filaments, out of the quenching apparatus. Although, for a circular array of filaments, the term "radial quench" is appropriate, the same system can work essentially similarly if the filamentary array is not circular, e.g., rectangular, oval, or otherwise, with correspondingly-shaped surrounding screen systems that direct the cooling gas inwards towards the filamentary array.

In the 1980's, Vassilatos and Sze made significant improvements in the high-speed spinning of polymeric filaments and disclosed these and the resulting improved filaments in U.S. Patent Nos. 4,687,610; 4,691,003; 5,034,182; 5,141,700; and more recently in 5,824,248 and copending applications 09/174,194 filed October 16, 1998 and 09/547,854 filed April 12, 2000. These patents disclose gas management techniques, whereby gas surrounds the freshly-extruded filaments to control their temperature and attenuation profiles. These types of quench systems and methods are known as pneumatic quench or spinning. Other pneumatic quenching methods include those described in U.S. Patent No. 5,976,431. Pneumatic spinning is a process which not only quenches the molten filaments, but also reduces the spinline tension, thereby providing better productivity and processability. In pneumatic spinning the cooling gas and filament traveling in the same

direction are passed through a conduit wherein the speed is controlled by a takeup roll. The tension and temperature are controlled by the gas flow rate, the diameter or cross-section of the conduit which controls the gas velocity, and the length of the conduit. The gas may be introduced at one or more locations along the conduit. Pneumatic quenching allows for spinning speeds in excess of about 5,000 mpm.

It has been found that for certain types of polymeric filaments cooled by some pneumatic quench systems, as the denier of the filament increases, the productivity and processability of the filament decreases, due to increased denier spread of the produced filaments. The increased denier spread is believed to be at least partially due to increased gas turbulence due to increased volumes of gas required for cooling the larger filaments in the pneumatic quench system, which increases non-uniformity of the filaments.

Thus, a need exists for a process, preferably a high-speed process, for producing melt-spun filaments having a low denier spread, and accordingly improved properties.

SUMMARY OF THE INVENTION

In accordance with these needs, there is provided a melt spinning process for spinning polymeric filaments, comprising passing a polymeric melt of a polymer formed from one or more chain-branching agents through a spinneret to form polymeric filaments, passing the filaments to a pneumatic quench zone, wherein a cooling gas is provided to the filaments to cool the filaments, wherein the cooling gas is directed to travel in the same direction as the direction of the filaments.

In accordance with these needs, there is also provided a melt spinning process for spinning polymeric filaments, comprising passing a polymeric melt of a polymer through a spinneret to form polymeric filaments having a denier per filament above about 4, passing the filaments to a quench zone, wherein a cooling gas is provided to the filaments to cool the filaments, wherein the cooling gas is directed to travel and accelerated in the same direction as the direction of the filaments, whereby a yarn formed from the produced filaments has a denier spread of less than 2.

In accordance with these needs, there is also provided a melt spinning process for producing polymeric filaments having a denier spread of below about 2, comprising passing a polymeric melt of a polymer having a laboratory relative viscosity above 22.5 through a spinneret to form polymeric filaments, passing the filaments to a quench zone, wherein a cooling gas is provided to the filament array to cool the filaments, wherein the cooling gas is directed to travel and accelerated in the same direction as the direction of the filaments.

In accordance with these needs, there is also provided a method of producing polyester yarn have a denier spread of less than about 2%, comprising forming filaments from a polyester having a laboratory relative viscosity above 22.5, and forming the filaments into a yarn.

There is also provided filaments, yarns, and other articles produced by these method.

Further objects, features and advantages of the present invention will become apparent from the detailed description that follows.

In accordance with these needs, there is provided a melt spinning process for spinning polymeric filaments, comprising passing a polymeric melt of a polymer formed from one or more chain-branching agents through a spinneret to form polymeric filaments, passing the filaments to a pneumatic quench zone, wherein a cooling gas is provided to the filaments to cool the filaments, wherein the cooling gas is directed to travel in the same direction as the direction of the filaments.

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There is also provided filaments, yarns, and other articles produced by these method.

10 Further objects, features and advantages of the present invention will become apparent from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Figure 1 is an illustration of a single stage pneumatic quenching system which may be used in the present invention.

Figure 2 is an illustration of a two-stage pneumatic quenching system which may be used in the
20 present invention.

Figure 3 is a graph illustrating the relationship between denier spread (DVA) and relative viscosity (LRV) for a 127 denier - 34 filament, round cross-section DMT polyethylene terephthalate polymer.

25 Figure 4 is a graph illustrating the relationship between denier spread (DVA) and relative viscosity (LRV) for a 265 denier - 34 filament, round cross-section DMT polyethylene terephthalate polymer.

30 DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method of making by pneumatic spinning a melt-spun polymeric filament having a low denier spread. The present invention also relates to a melt-spun polymeric

filament having a low denier spread made by the method of the invention described herein.

The present inventors have found that increasing
5 the viscosity of the polymer to be spun can reduce the denier spread of the produced filament, thereby overcoming the problem of high denier spread found in other processes.

The term "filament" is used herein generically,
10 and encompasses cut fibers (often referred to as staple), although synthetic polymers are generally prepared initially in the form of continuous polymeric filaments as they are melt-spun (extruded). A group of filaments are combined to form a yarn. The method of
15 the invention may be used to make any type of yarn, such as fully drawn yarn, partially oriented yarn (POY), or staple. Preferably, the yarn made is partially oriented for later texturing by methods known in the art. Any desired texturing methods may be used
20 including false twist texturing, air jet texturing, and draw-texturing.

The filaments may be produced to have any desired cross-section including round, oval, trilobal, and scalloped oval. Any melt-spinnable polymer can be used
25 in the present process; including polyesters and polyolefins. Preferably the polymer is a polyester. The polyester can be a homopolymer, copolymer, mixture of polyester, bicomponent, or chain-branched polyester. Useful polyesters include polyethylene
30 terephthalate ("2-GT"), polytrimethylene terephthalate or polypropylene terephthalate ("3-GT"), polybutylene terephthalate ("4-GT"), polyethylene naphthalate, poly(cyclohexylenedimethylene) terephthalate, poly(lactide), poly(ethylene azelate), poly(butylene

terephthalate), poly[ethylene(2,7-naphthalate)],
poly(glycolic acid), poly(ethylene succinate),
poly(ethylene adipate), poly(ethylene sebacate),
5 poly(ethylene sebacate), poly(decamethylene adipate),
poly(decamethylene sebacate), poly(.alpha.,.alpha.-
dimethylpropiolactone), poly(para-hydroxybenzoate)
(akono), poly(ethylene oxybenzoate), poly(ethylene
isophthalate), poly(tetramethylene terephthalate),
10 poly(hexamethylene terephthalate), poly(decamethylene
terephthalate), poly(1,4-cyclohexane dimethylene
terephthalate) (trans), poly(ethylene 1,5-naphthalate),
poly(ethylene 2,6-naphthalate), poly(1,4-
cyclohexylidene dimethylene terephthalate)(cis), and
15 poly(1,4-cyclohexylidene dimethylene
terephthalate)(trans).. Methods of making the polymers
used in the present invention are known in the art and
may include the use of catalysts, co-catalysts, and
chain-branchers to form the copolymers and terpolymers,
20 as known in the art.

For example, a suitable polyester may contain in
the range of about 1 to about 3 mole % of ethylene-M-
sulfo-isophthalate structural units, wherein M is an
alkali metal cation, as described in U.S. Patent No.
25 5,288,553, or 0.5 to 5 mole% of lithium salt of
glycollate of 5-sulfo-isophthalic acid as described in
U.S. Patent No. 5,607,765. Filaments of the invention
can also be formed from any two polymers as described
above into so-called "bicomponent" filaments, arranged
30 side-by-side or in a sheath-core arrangement.
Especially useful is polyethylene terephthalate (PET).
The PET can be prepared by either the DMT or TPA
process as described below. Also useful are chain
branched polymers which are discussed in detail below.

The process of the invention produces yarns of useful denier spread. Denier spread (DVA) is a measure of the along-end denier variability of a yarn by calculating the variation in mass at regular intervals along the yarn. Denier variability is measured by running yarn through a capacitor slot, which responds to the instantaneous mass in the slot. The test sample is electronically divided into eight 30 m subsections with measurements every 0.5 m. Differences between the maximum and minimum mass measurements within each of the eight subsections are averaged. Denier spread is recorded as, % DVA, a percentage of the averaged difference divided by the average mass along the whole 240 m of the yarn. Testing can be conducted on an ACW400/DVA (Automatic Cut and Weigh/Denier Variation Accessory) instrument available from Lenzing Technik, Lenzing, Austria, A-4860.

A low denier spread is desirable, as non-uniformities in a filament may present problems in the downstream processing of the filament. Additionally, low denier spread permits high texturing speeds, evenness of coloration, and uniformity of bulk or cover in fabrics formed from the filaments. The present process can provide yarns having a DVA of less than about 2.0, preferably less than about 1.5, more preferably less than about 1.2, and most preferably less than about 1.0. As shown in Figures 3 and 4, the lower the dpf, the lower the denier spread that can be obtained, keeping other conditions the same.

The yarn can be formed from any desired number of filaments. If the dpf is above 5, then preferably the yarn is formed from about 5 to about 200 filaments,

more preferably about 8 to about 100, most preferably about 10 to about 70 filaments.

In some embodiments of the invention, the
5 filaments have a dpf above about 3.4 dpf, preferably in the range of about 3.5 to about 15.0, more preferably about 4.0 to about 12, most preferably about 5.0 to about 9.0 dpf. However, the present invention not only relates to lowering the denier spread of high denier
10 filament yarns, but also relates to decreasing the denier spread of a low denier filament yarn, e.g. those with a dpf less than about 3.5, less than about 2.0, or less than about 1.0, which may already exhibit an acceptable denier spread. Regardless of the dpf, the
15 full range of DVA discussed above can be obtained by appropriate selection of process conditions, such as speed and polymer viscosity.

The present inventors have found that the denier spread is related to the viscosity of the polymer. As
20 illustrated in the Examples and as shown in Figures 3 and 4, as the relative viscosity increases, the denier spread of the polymeric filament decreases. Therefore, a polymer should be chosen with a high enough LRV to give acceptable DVA. The melt viscosity can be
25 increased by any desired method, such as using a chain branching agent to form the polymer, or forming the initial polymer with a higher viscosity by use of other polymerization techniques known in the art, such as polymerizing further to increase polymer chain length.

30 Additionally, as explained in Example 2, pneumatic spinning and the use of a chain branching agent can have a synergistic effect in reducing denier spread, while allowing for the use of high speed, thereby increasing productivity. Thus, the invention also

relates to increasing the productivity of a polymeric filament production by adding a chain branching agent and pneumatically spinning the filament.

- 5 Any chain branching agents which can increase the melt viscosity of the polymer to give the desired denier spread can be used. The chain branches can be added during the formation of the initial polymer or afterward to increase the viscosity to desired levels.
- 10 Chain branching agents are any agents that react with the monomer(s) or polymer to increase the viscosity of the polymer. They are generally multifunctional compounds, containing three or more functional groups such as hydroxyl, carboxyl, or ester groups. Suitable
- 15 chain branching agents include trimethyl trimellitate, pentaerythritol, trimer acid, mellitic acid, trimethylolpropane, trimethylolethane, glycerine, trimesic acid and trifunctional esters thereof, trimethylolpropane, tetraethyl silicate, pyromellitic
- 20 acid, phloroglucinol, hydroxyhydroquinone, and other chain branching agents known in the art. Preferred chain branching agents are those that are adequately stable in monomer form during processing and polymerization and in polymeric form during formation,
- 25 spinning, and further processing. See U.S. Patent Nos. 3,576,773; 4,092,299; 4,113,704; 4,945,151; 5,034,174 and 5,376,735, and Journal of Applied Poly. Science (Vol. 74 pp. 728-734, 1999), all of which are incorporated herein by reference, for descriptions of
- 30 useful chain-branchers. The chain-polymers can be made by techniques known in the art. In a preferred embodiment of the invention, the chain branching agents includes trimethyl trimellitate.

In the embodiments of the invention wherein the polymeric filament is a polyethylene terephthalate polyester, the filament may be prepared by any suitable synthetic pathway known in the art. In particular, the filament may be prepared by either of the two main synthetic pathways for preparing polyethylene terephthalate polyesters which are (1) "DMT", the ester interchange of dimethyl terephthalate with ethylene glycol, and (2) "TPA", the reaction of terephthalic acid with ethylene glycol. Any suitable chain branching agent known in the art may be used in either synthetic pathway. DMT polymers often have a suitably high viscosity without addition of chain branches, due to the impurities inherent in the DMT process that give rise to branches, thus increasing viscosity. The chain-branchers of the present invention are additional functional compounds added to the process, not those inherent in DMT or TPA method. In a preferred embodiment wherein the chain branching agent is trimethyl trimellitate, the polyethylene terephthalate may be made by either the DMT or the TPA pathway.

Any suitable amount of the chain branching agent may be used in the polymer used in the present invention. A suitable amount is an amount which effectively increases the relative viscosity of the polymer to the relative viscosity which corresponds to the desired denier spread. This is a function of the dpf of the filament, as well as the type of polymer; and the process parameters such as spinning speed. For example, if a denier spread of about 1.0% is desired for the filaments represented in Figure 3, then the effective amount of the chain branching agent will be that which increases the relative viscosity of the

polymeric filament to about 23.3 LRV. For example, about 100 to about 10,000 ppm of crosslinks can be used. In a preferred embodiment wherein the chain
5 branching agent is trimethyl trimellitate, the polymer is polymerized using about 0.085 to about 0.23% by weight of the trimethyl trimellitate (on the weight of the polymer) or about 3.4 to about 9.1 microequivalent crosslinker per gram of polymer.

10 No chain branching agent is needed if a polymer is chosen with high enough LRV and filaments of low enough dpf are made to obtain a suitable DVA. Preferably, the LRV of the polymer, whether or not chain-branched is greater than about 22.0, or greater than about 22.5 or
15 greater than about 23.0 to give the desired denier spread.

In the process of the invention, the polymer is melt-spun through a spinneret using known techniques. The spun filaments are then quenched by pneumatic
20 methods. Generally, pneumatic quenching involves supplying a given volume of cooling gas to cool the polymeric filament. Any gas may be used as a cooling medium. The cooling gas is preferably air, because air is readily available, but other gases may be used, for
25 instance steam or an inert gas, such as nitrogen, if required because of the sensitive nature of the polymeric filaments, especially when hot and freshly extruded.

In pneumatic spinning the cooling gas and filament
30 are passed through a conduit wherein the speed is controlled by a takeup roll. The tension and temperature are controlled by the gas flow rate, the diameter or cross-section of the conduit which controls the gas velocity, and the length of the conduit. The

gas may be introduced at one or more locations along the conduit. Preferably, the gas is accelerated through or out of the quench zone by the use of a
5 converging or tapered section, or by use of a tube of restricted volume.

Pneumatic quenching allows for spinning speeds in excess of about 3,000 mpm, e.g. above 4,000 mpm, or above 5,000 mpm. Examples of suitable pneumatic
10 spinning methods and systems, which may be used, are disclosed in U.S. Patent No. 5,824,248 ('248 patent), which is incorporated herein by reference and U.S. Serial No. 09/547,854 filed April 12, 2000, which is also incorporated herein by reference. Any of the
15 pneumatic methods, described in the background section can be used. Preferred embodiments include a single stage method as illustrated in the '248 patent and a two-stage method of 09/547,854. An exemplary single stage method is illustrated in Figure 1 and an
20 exemplary two-stage method is illustrated in Figure 2.

While the devices of Figures 1 and 2 are annular, they can be adopted to other shapes. As shown in Figure 1, the single stage pneumatic quench apparatus includes a cylindrical housing 50 which forms an
25 annular chamber 52 that is supplied with pressurized cooling gas blown in through an inlet conduit 54 which is formed in an outer cylindrical wall 51 of the housing 50. The annular chamber 52 has an annular bottom wall 53 attached to a cylindrical inner wall 66,
30 at the lower portion of the annular chamber 52, below a cylindrical quench screen system 55 that defines the inner surface for the upper portion of the annular chamber 52 and through which the pressurized cooling gas is blown radially inwards from the annular chamber

52 into a zone 18 below a spinneret face 17 through which zone 18 passes a bundle of filaments 20 which are still molten, having been freshly-extruded from a heated melt in a heated spinning pack 16 through holes (not shown) in the spinneret face 17 which is centrally located with respect to the housing 50 and is recessed from the face 16a (of the spinning pack 16) onto which the housing 50 abuts. Filaments 20 continue from zone 18 out of the quenching system through a tube formed by the inner wall 66 that surrounds the filaments, down to a puller roll 34, the surface speed of which is termed the withdrawal speed of the filaments 20.⁴

Proceeding down below the cylindrical quench system 55, the filaments may pass, effectively, through a short tube 71 of the same internal diameter as the cylindrical quench system 55, and pass preferably through a tapered section 72, before entering a tube 73 of smaller internal diameter and extending below the bottom 53 of the housing 50. The relative speeds of the gas and filaments can be varied to give desired results. The filaments 20 will preferably have already hardened before they leave the tube 73, in which case, when they leave the tube 73, their speed will already be the same speed as their withdrawal speed at the roll 34.

Providing a tapered entrance 72 to the tube is optional but preferred. It is believed that an appropriately-tapered entrance to the tube smoothes the acceleration of the cooling gas, and may reduce turbulence. Tapered entrances to tubes have been used, with taper angles of 30°, 45° and 60°, the optimum taper angle depending on a combination of factors. A tube of about 1 inch (2.5 cm) diameter has been found very

useful in practice. A tube of about 1.25 inches (3.2 cm) diameter has also been used effectively. It is preferable that the top of the tube is not spaced too far from the spinneret. The top of the tube should be spaced about 80 cm or less from the top of the tube, and preferably less than about 64 cm.

The shape of the tube 73 that is of restricted dimensions need not only be of cylindrical cross-section, but may vary, especially when a non-circular array of filaments is extruded. Thus, for instance, tubes of rectangular, square, oval or other cross-section may be used.

The following dimensions are shown in Figure 1:

A - Quench delay height, the height of the spinneret face 17 above the face 16a;

B - Quench screen height, the height of the cylindrical quench screen system 55 (extending from the face 16a to the top of the inner wall 66); and

C₁ - Connecting tube height, the height of short tube 71;

C₂ - Connecting taper height, the height of tapered section 72; and

C₃ - Tube height, the height of the tube 73 of restricted diameter that causes the cooling gas to accelerate out of the zone 18.

In Figure 1, the filaments 20, after leaving the quench system, continue down to the driven roll 34 which pulls the filaments 20 in their path from the heated spinneret so their speed at the roll 34 is the same as the surface speed of the driven roll 34 (disregarding slippage), this speed being known as the withdrawal speed. As is conventional (but not shown in the drawings) a finish is generally applied to the

solid filaments 20 before they reach the driven roll 34.

As shown in Figure 2, the pneumatic quenching system may comprise two stages, e.g. introduce gas to the filaments in two-locations, a converging section 116 for accelerating the air, and a converging/diverging section in tube 119. A first stage chamber 105 and a second stage chamber 106 are each formed in the cylindrical inner wall of the housing 107. The first stage chamber 105 is adapted to be located below a spinneret 113 and supplies gas to the filaments 114 to control the temperature of the filaments 114. A second stage chamber 106 is located between the first stage gas inlet 108 and a tube 119 located below the first gas flow inlet 108 for surrounding the filaments 114 as they cool. An annular wall 102, which is attached to cylindrical inner wall 103 at the lower portion of the first stage chamber 105, separates the first stage chamber 105 from the second stage chamber 106.

A first stage gas inlet 108 supplies gas to the first stage chamber 105. Similarly, a second stage gas inlet 109 supplies gas to the second stage chamber 106. Note that there can be a single gas inlet supplying one or more chambers; and the number of gas inlets can be modified to allow flexibility in controlling gas flow. The cooling gas flowing to each stage can be regulated independently by supplying pressurized cooling gas through inlets 108 and 109, respectively.

A cylindrical quench screen assembly 111, comprising one or more parts, preferably a cylindrical perforated tube and a wire screen tube, is centrally positioned in the first stage chamber 105. The

"perforated tube" is a means for distributing gas flow radially into a stage. Pressurized cooling gas is blown inwards from first stage inlet 108 through first stage chamber 105 and through the cylindrical quench screen assembly 111 into a zone 112 formed in the interior cylindrical wall of the cylindrical quench screen assembly 111, below spinneret 113. A bundle of molten filaments 114, after being extruded through spinneret holes (not shown), pass through zone 112 where the filaments 114 begin to cool. An inner wall 103 is disposed below the cylindrical quench screen assembly 111 and between the first stage gas inlet 108 and the second stage gas inlet 109. A first stage converging section 116 is formed in the interior of housing 107, and more specifically in the interior wall of inner wall 103, between the first stage gas inlet 108 and the second stage gas inlet 109. The converging section can be located in any portion of the apparatus, such that it accelerates the air speed. The converging section can be moved up or down the tube to achieve the desired gas management. There can be one or more such converging sections. The filaments 114 continue from the zone 112 out of the first stage of the quenching system through a short tubular section of the inner wall 103 before passing through the first stage converging section 116, along with the first stage cooling gas, which accelerates in the filament travel direction as the filaments 114 continue to cool.

30 A cylindrical perforated tube 117 is disposed below the first stage converging section 116 and between the first stage gas inlet 108 and the second stage gas inlet 109. The cylindrical perforated tube 117 is located centrally within the second stage

chamber 106. However, the perforated tube 117 can be located as desired to provide the desired gas to the filaments for example, below the second stage gas inlet. A cylindrical inner wall 118 is located below the cylindrical perforated tube 117. A second supply of cooling gas is provided from the second stage supply inlet 109 by forcing the gas through the cylindrical perforated tube 117. Between the first and second stage converging sections, 116 and 126 respectively, is a tubular section 125 formed by the inner walls of the converging section 116 of the entrance diameter D3, exit diameter D4 and height L2. The tubular section 125 and the converging section 116 can be formed as a single piece or formed as separate pieces that are connected together, for example by threading.

The tubular section 125 may be straight as shown in Figure 2 or tapered. The ratio of diameters D2 to D4 is generally $D4/D2 < 0.75$ and preferably $D4/D2 < 0.5$. By use of such a ratio, the speed of the cooling air can be increased. The second stage cooling gas passes through the second stage converging section entrance 126, with diameter D5 created by the exit of tubular section 125 of the first converging section 116 and the entrance of the spinning tube 119. The term spinning tube is used to refer to that portion of the apparatus having a converging/diverging arrangement." Preferably, the last portion of the tube has such an arrangement. The upper end of the spinning tube 119 is located in the interior surface of the cylindrical inner wall 118.

A second stage converging section 126 of length L3 and an exit diameter D6 is formed in the interior wall of tube 119, and is followed by a diverging section 127 of length L4, also formed in the interior wall of the

tube 119, which extends to the end of the tube 119, which has an exit diameter D7. The filaments 114 leave the tube 119 through the exit diameter D7 and are taken up by a roll 104 whose surface speed is termed the withdrawal speed of the filaments 114. The speed may be modified as desired. Preferably, the roll 104 is driven at a surface speed of above 3,500 mpm. The average velocity of the combined first and second stage gases increases in the filament travel direction in the second stage converging section 126 and then decreases as the cooling gas moves through the diverging section 127. The second stage cooling gas combines with the first stage cooling gas in the second stage converging section 126 to assist with filament cooling. Cooling gas temperature and flow to inlets 108 and 109 may be controlled independently.

An optional converging screen 120, or diffuser cone, having perforated walls, may be located at the exit of spinning tube 119. Cooling gas is allowed to exhaust through the perforated walls of the diffuser cone 120, which reduces the exit gas velocity and turbulence along the filament path. Variations of the diffuser cone 120 may be utilized to reduce the turbulence exerted on the filaments 114. The filaments 114 may leave the spinning tube 119 through the exit nozzle 123 of the converging screen 120 and from there the filaments 114 may be taken up by a roll 104.

The following dimensions are shown in Figure 2:

30 A - Quench delay height is the difference between the spinneret face and the pump-block bottom surface 122 against which the housing 107 abuts;

B - Quench screen height is the vertical length of the cylindrical quench screen assembly 111;

- L1 - First stage converging section length;
L2 - First stage tube length;
D2 - First stage converging section entrance
5 diameter;
D3 - First stage converging section tubular
section entrance diameter;
D4 - First stage converging section tubular
section exit diameter;
10 D5 - Second stage converging section entrance
diameter;
D6 - Second stage converging section exit
diameter;
D7 - Second stage diverging section exit diameter;
15 and
L5 - Optional converging screen length.

Gas may be introduced in 108 and 109,
independently at atmospheric or increased pressure.
Also, gas may be forced into the first stage gas inlet
20 108 above atmospheric pressure allowing gas to be
sucked into the second stage gas inlet 109. The same
or different gases may be introduced in the first and
second stage gas inlets 108 and 109.

Variations of the two-stage apparatus can be used
25 as described in U.S. Serial No. 09/547,854. For
example, the apparatus can have two or more gas inlets,
and one or more gas outlets. Also, tube 119 can be a
straight tube, and not include the converging/diverging
section. It is only important that the apparatus have
30 at least one converging section to accelerate the
cooling gas.

The delay A in Figure 6 can be an unheated or
heated delay (often termed an annealer). The length

and temperature of the delay may be varied to give desired cooling speed of the filaments.

After quenching, the filaments are converged,
5 interlaced, and wound as a multi-filament bundle using techniques known in the art. Any desired wind-up method can be used such as winding by use of friction driven winders or spindle drive-winders. For example, yarn can be wound on a multi-end, automatic transfer,
10 turret windup manufactured by Barmag AG (Remscheid-Lennep, Germany).

The produced filaments can be formed into multi-filaments, yarns, fabrics, and other articles.

The properties used to characterize the filaments
15 of the present invention were measured as follows:

Draw tension (DT), in grams, is measured at a draw ratio of 1.7 times, and at a heater temperature of 180° C. Draw tension is used as a measure of orientation. Draw tension may be measured on a DTI 400 Draw Tension
20 Instrument, also available from Lenzing Technik.

Tenacity (Ten) is determined as the load in grams at the point of failure and divided by the denier. Elongation (% E) is the percent increase in length of the yarn at the point of failure. Ten and % E are
25 measured according to ASTM D2256 using a 10 in (25.4 cm) gauge length sample, at 65% RH and 70 ° F., at an elongation rate of 60% per min.

DVA % is measured as discussed earlier.
Q1/Q2 are volumetric air flows measured in cubic feet
30 per minute (CFM) to chambers 105 and 106 of Fig. 2 measured using a Brandt B-NZP 1000 Series Gas Flow Sensor.

%U was measured as follows: An Uster Tester 3 Model C manufactured by Zellweger Uster AG CH-8610,

Uster, Switzerland may be used to measure the test yarn evenness U% or linear irregularity of mass value. The percent indicates the amount of mass deviation from the mean mass of the tested sample and is a strong indicator of the overall material uniformity. Testing may be done following the ASTM Method D 1425. The tester's Rotofil twister unit was set to provide S twists to the yarn and its pressure adjusted to get optimum U%.

U%CV is the square root of the variance of the mass variations normalized by the mass mean value and expressed as a percentage. Like evenness it is a measure of yarn along-end mass or denier variability.

Laboratory relative viscosity (LRV) measures the ratio of the absolute viscosity of a polymer solution to the absolute viscosity of the solvent, or the ratio of the efflux times of the polymer solution and the solvent in a Cannon-Fenske viscometer (size 200) at 25 C. The polymer solution was an 8% weight/volume (4.75% weight/weight) concentration at 25 C. The solvent used is hexafluoroisopropanol containing 100 ppm sulfuric acid.

Denier or linear mass is the weight in grams of 9000 meters of yarn. Denier is measured by forwarding a known length of yarn, usually 45 meters, from a multifilament yarn package to a denier reel and weighing on a balance to an accuracy of 0.001 g. The denier is then calculated from the measured weight of the 45 meter length. Yarn denier was measured using the Lenzing Technik ACW 400/DVA (Automatic Cut and Weigh/Denier Variation Accessory) instrument. P1/P2 in H₂O are the first stage and second stage pressure respectively, measured at the walls of

chambers 105 and 106 in Fig. 2 using an Alnor Model S30 micromanometer. P1/P2 are actual gauge pressures relative to atmospheric.

5 Block temperature is the temperature of the Dowtherm heating vapor within the heating cavities surrounding the metal block for polymer transport between the spinning meter pump and the spinning pack.

 Polymer temperature is a thermocouple reading of
10 the polymer temperature in the melt pool before the spinneret plate.

 The invention is further illustrated by the following non-limiting examples.

15

EXAMPLES

Example 1

The Effect of Polymer Viscosity on Denier Spread For Low and High Denier Filaments

20 In this experiment, a two-stage pneumatic quenching system, as described above and illustrated with reference to Figure 2, was used to melt-spin the following commercially available polyethylene terephthalate polymers prepared by the DMT process: (1)
25 a 127 denier - 34 filament (127-34) having a relative viscosity (LRV) of 23.3, (2) a 127 denier - 34 filament (127-34) having an LRV of 21.8, (3) a 265 denier - 34 filament (265-34) having an LRV of 23.3, and (4) a 265 denier - 34 filament (265-34) having an LRV of 21.8.
30 The filaments had a round cross-section. The polymers used were DMT Crystar 3956 (3956) and DMT Crystar 3915 (3915) available from E.I. DuPont Crystar, Old Hickory, TN. The filaments produced were partially oriented.

The pertinent processing parameters used and the filament characteristics are shown in Table 1. The other features of the quenching apparatus are as described in Example 1 of U.S. Serial No. 09/547,854. Examples B, D, and F are comparative examples demonstrating the adverse effects low viscosity has on denier spread. The first pair, filaments A and B, is a comparison which shows that for a 127 denier - 34 filament, as the relative viscosity increases, the denier spread (DVA) decreases. This relationship is graphically represented in Figure 3 as denier spread % vs. relative viscosity.

The second pair, filaments C and D, is a comparison which shows that for a 265 - 34 filament, as the relative viscosity increases, the denier spread decreases.

The second pair may also be compared with the third pair, filaments E and F, to illustrate that lower spinning speeds may be used to achieve an even lower denier spread. E and F are graphically represented in Figure 4 as denier spread % vs. relative viscosity. Thus, increasing LRV may slightly reduce the spinning speed that can be used (yet still higher than traditional processes), but greatly reduces the denier spread.

Table 1
Effect of Relative Viscosity

Count	Polymer Type	LRV	Spin Speed (rpm)	Draw Tension (g)	DVA %	Ten, gpd/ Elong (%)	U%	U%CV	Block/ Poly T, °C	P1/P ₂ , in. H ₂ O	Q1/Q2	Stage 1 Tube length (L2) X ID (D2→D3)	Screen tube length (B)
A 127-34	3956	23.3	4380	62.4	1.00	2.57/125.1	1.32	1.65	305.0/307.7	7.0/3.5	53/70	3" x 1" →0.75"	6.5"
B 127-34	3915	21.8	4515	59.0	1.50		—	—	305.0/309.8	7.0/3.5	53/70	3" x 1" →0.75"	6.5"
C 265-34	3956	23.3	4310	121.7	1.67	2.38/121.9	1.48	1.85	282.0/293.8	4.0/3.5	56/45	6"x1"	6.5"
D 265-34	3915	21.8	4480	129.2	3.63		—	—	274/292.0	4.0/3.5	56/45	6"x1"	6.5"
E 265-34	3956	23.3	4180	127.3	1.41	2.45/119.9	1.18	1.48	278/291.9	3.5/3.5	52/40	6"x1"	6.5"
F 265-34	3915	21.8	4330	125.3	3.6	2.25/117.4	1.54	1.94	274/291.8	3.5/3.5	52/40	6"x1"	6.5"

Example 2The Effect of Polymer Viscosity on Denier Spread For
High Denier Filaments

To show the effect of increasing viscosity on the
5 denier spread of high denier polymeric filaments,
polymers were melt-spun by a two-stage pneumatic
quenching process as described above and illustrated
with reference to Figure 2. The first four polymers
were quenched on an apparatus described in Example 1
10 of U.S. Serial No. 09/547,854. The fifth polymer was
spun on the same apparatus, but with a 6" by 1" stage
1 cone, so the first stage tube height L₂ is 6. The
following four commercially available polyethylene
terephthalate polymers were formed into 265 denier -
15 34 filament, round cross-section polymeric filaments:
(1) a TPA polyethylene terephthalate (PET) polymer
obtained from Yizheng, Yizheng Chemical Fibre Co.,
Ltd, P.R. China, (2) a DMT Crystar 3956 polymer, (3) a
TPA polyethylene terephthalate polymer obtained from
20 Dupont Suzhou Polyester Co., Ltd. New District, Suzhou
Jiangsu, P.R. China, and (4) a second DMT Crystar 3956
PET polymer. A polyethylene terephthalate polymer was
polymerized using the TPA polymerization route in the
DuPont Polyester Technologies' Technical Laboratory
25 and a chain branching agent, trimethyl trimellitate,
in an amount of about 856 ppm was also used. All the
Crystar polymers were obtained from E.I. DuPont
Crystar, Old Hickory, Tennessee.

The pertinent processing parameters used and the
30 filament characteristics are shown in Table 2. The
table shows increasing viscosity without a chain
branching agent provides reduced denier spread. All
the filaments were partially oriented, and intended

for further texturing. As seen in Table 2, the use of a chain branching agent allows for good denier spread to be obtained, while high speeds can be maintained, since it is not necessary to increase the viscosity as much as if no chain branching agent were used.

Specifically, the TPA polyethylene terephthalate polymer with the chain branching agent provides a polymeric filament having a low denier spread, about 1.61 % DVA. This denier spread is lower than that obtained with both the TPA and DMT polyethylene terephthalate polymers without a chain branching agent, even those with a higher LRV than the chain branched polyester. Additionally, as shown in Table 2, the TPA polyethylene terephthalate polymer with the chain branching agent may be melt-spun at higher spinning speeds, yet still provide a filament with a low denier spread.

Table 2
Effect of Chain Branching Agent on Denier Spread

Polymer Type (all 265/34)	LRV	Spin Speed (mpm)	Drawn Ten (g)	DVA %	Ten, gpd/ Elong (%)	U%	U% CV	Block/Poly T °C	P ₁ /P ₂ in. H ₂ O	Q ₁ /Q ₂ CFM.END	Stage1 tube length x ID
TPA Yizheng	21.3	4200	99.2	2.85	—	—	—	287/294.5	1.6/3.0	38/37	3" x 1"
DMT Crystar 3956	23.3	4200	143.3	1.85	—	—	—	287/300.1	1.6/3.0	38/37	3" x 1"
TPA Suzhou	21.7	4310	129.8	2.62	—	2.46	3.03	287/297.4	2.0/2.0	41/23	3" x 1"
DMT Crystar 3956	23.3	4360	125.0	1.87	2.33/119.72	1.23	1.54	287/300.7	3.0/2.0	53/35	3" x 1"
TPA with Chain Branching Agent	22.9	4775	158.3	1.61	2.34/127.20	1.00	1.26	278/295.5	4.5/3.5	60/45	6" x 1"

Example 3Effect on Draw Tension %CV for Single Stage Pneumatic
Quench

To determine the effect of using a chain branching agent and pneumatic quenching, filament were produced using a single stage quenching system as described above and illustrated with reference to Figure 1. 127 denier - 34 filament polyethylene terephthalate filaments were obtained by using the pneumatic spinning system to spin (i) a DMT PET homopolymer from Crystar and (ii) PET including a chain branching agent. The PET with the chain branching agent was the same as that used in Example 2.

For the first filament as shown in Table 3, the pneumatic quench system as illustrated in Figure 1 was used with A=1.0", B=5.5", C1=2.5", C2=2.0", C3=15.0", and the spinneret tube exit =26.0" and tube 73 = 1.0". For the second filament as shown in Table 3, the pneumatic quench system as illustrated in Figure 1 was used with A=1.0", B=5.5", C1=3.0", C2=0.0", C3=15.0", spinneret to tube exit = 24.5, and tube 73 =1.0".

The pertinent processing parameters used and the filament characteristics are shown in Table 3. As illustrated in Table 3, the use of a chain-brancher to produce the polymers that are formed into the filaments, produces significantly reduced %CV, and allowed for higher spinning speed. The %CV is defined as the square root of the sample variance normalized by the sample mean and expressed as a percentage. The sample mean is determined by the sum of individual observations divided by the total sample count. Thus, a lower %CV, means the filaments are more uniform. Thus, the use of a crosslinker to increase viscosity,

gives a more uniform product in the single stage pneumatic system.

Table 3						
Effect of Pneumatic Quenching and Chain Branching Agent on Productivity						
Chain Branching Agent	Spin Speed (mpm)	Draw Ten (g)	Draw Tension %CV	Polymer Temperature (°C)	Gms/min per hole	Q ₁ CFM
NO	3922	60.7	2.09	294.3	1.62	30
YES	4157	59.1	1.53	303.2	1.72	30

5 Although the invention has been described above in detail for the purpose of illustration, it is understood that the skilled artisan may make numerous variations and alterations without departing from the spirit and scope of the invention defined by the

10 following claims.

CLAIM(S)What is claimed is :

- 5 1. A melt spinning process for spinning polymeric filaments, comprising passing a polymeric melt of a polymer formed from one or more chain-branching agents through a spinneret to form polymeric filaments,
- 10 passing the filaments to a pneumatic quench zone, wherein a cooling gas is provided to the filaments to cool the filaments, wherein the cooling gas is directed to travel in the same direction as the direction of the filaments.
- 15 2. A process as claimed in claim 1, wherein the cooling gas is provided to the filaments in a single stage and passes through a tapered section and a zone of restricted dimensions to accelerate the gas.
- 20 3. A process as claimed in claim 1, wherein the cooling gas is provided to the filaments in two stages, and wherein the gas is accelerated by a converging section in the quench zone.
- 25 4. A process as claimed in claim 1, further comprising gathering the filaments to form a yarn.
- 30 5. A process as claimed in claim 1, wherein the polymer comprises a polyester.
6. A process as claimed in claim 1, wherein the polymer comprises polyethylene terephthalate.

7. A process as claimed in claim 1, wherein the chain branching agents comprise a tri or higher functional acid, alcohol, or ester.
- 5 8. A process as claimed in claim 1, wherein the chain branching agent comprises trimethyl trimellitate.
9. A process as claimed in claim 1, wherein a yarn formed from the produced filaments has a denier spread
10 of less than about 2 and the filaments have a denier per filament of greater than about 4.
10. A process as claimed in claim 1, wherein a yarn formed from the produced filaments has a denier spread
15 of less than about 1.5 and a denier per filament of less than about 4.
11. A process as claimed in claim 1, wherein the polymer has a laboratory relative viscosity of above
20 22.
12. A process as claimed in claim 1, wherein the filaments travel through the quench zone at a speed of greater than about 3,500 meters per minute.
25
13. A process as claimed in claim 1, wherein the filaments travel through the quench zone at a speed of greater than about 4,000 meters per minute.
- 30 14. Filaments produced by the process of claim 1.
15. An article formed from the filaments of claim 14.

16. A melt spinning process for spinning polymeric filaments, comprising
- 5 passing a polymeric melt of a polymer through a spinneret to form polymeric filaments having a denier per filament above about 4,
- passing the filaments to a quench zone, wherein a cooling gas is provided to the filaments to cool the filaments, wherein the cooling gas is directed to travel and accelerated in the same direction as the
- 10 direction of the filaments,
- whereby a yarn formed from the produced filaments has a denier spread of less than 2.
17. A melt spinning process as claimed in claim 16,
- 15 wherein the filaments have a denier per filament above about 5.
18. A melt spinning process as claimed in claim 16,
- wherein the polymer comprises polyethylene
- 20 terephthalate.
19. A melt spinning process for producing polymeric filaments having a denier spread of below about 2, comprising
- 25 passing a polymeric melt of a polymer having a laboratory relative viscosity above 22.5 through a spinneret to form polymeric filaments,
- passing the filaments to a quench zone, wherein a cooling gas is provided to the filament array to cool
- 30 the filaments, wherein the cooling gas is directed to travel and accelerated in the same direction as the direction of the filaments.

20. A method of producing polyester yarn have a denier spread of less than about 2%, comprising forming filaments from a polyester containing one or more chain-branching agents having a laboratory relative viscosity above 22.5, and forming the filaments into a yarn.

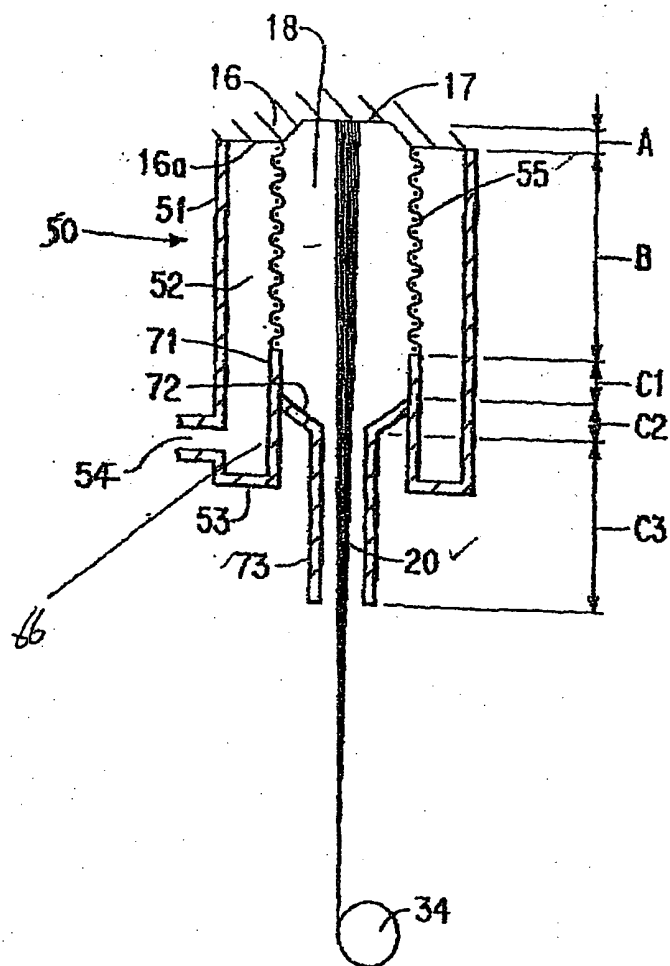


Fig. 1

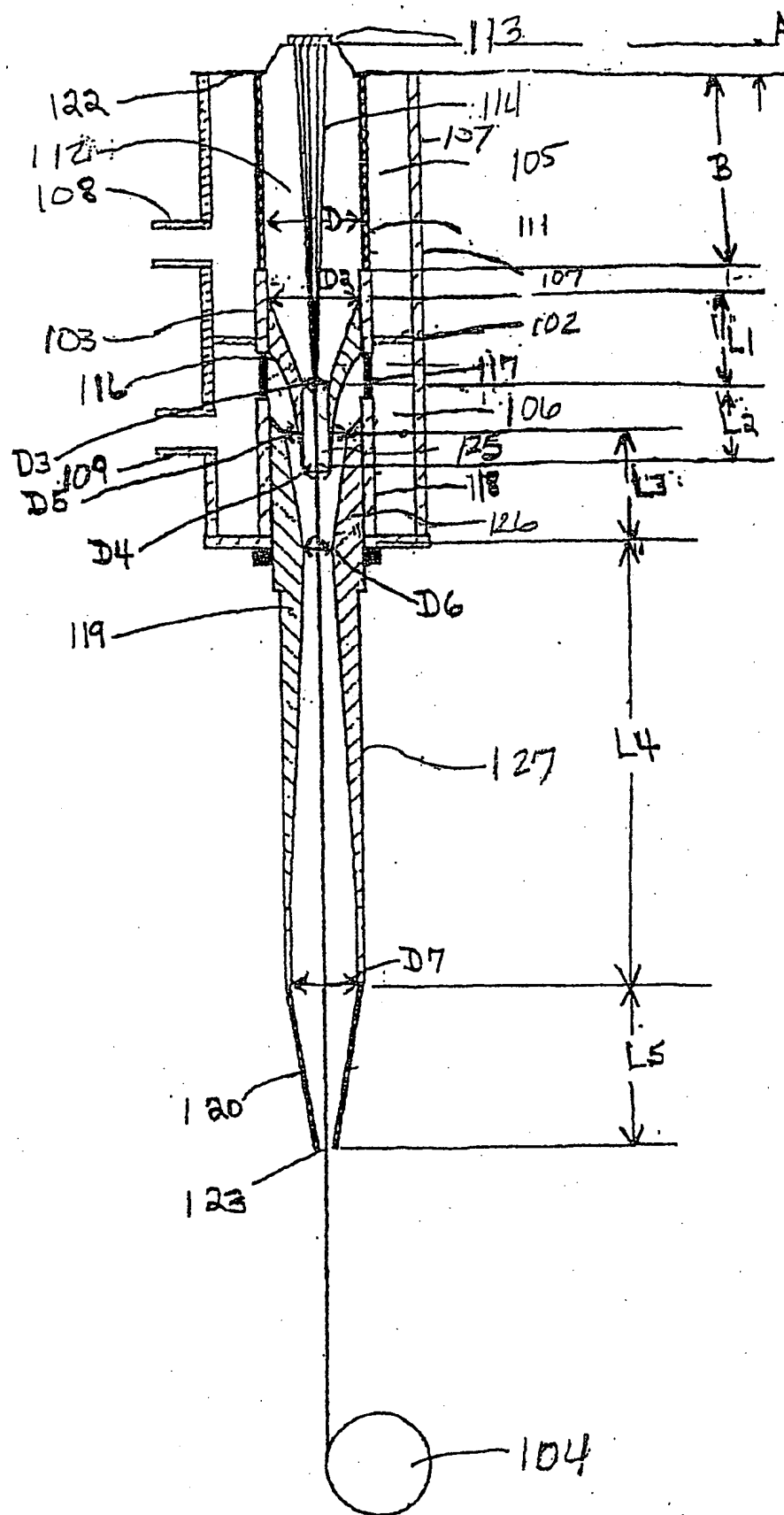


Fig. 2

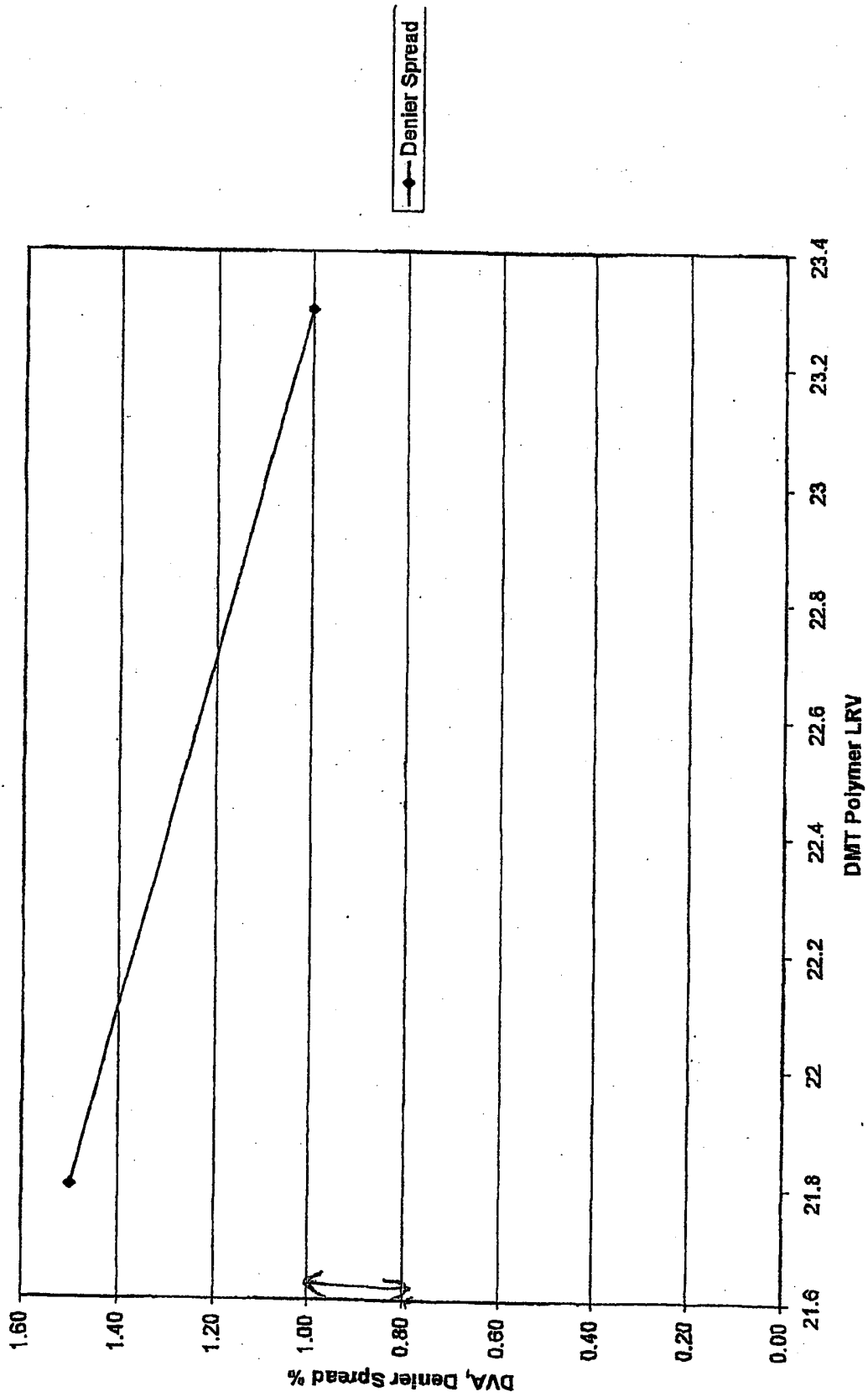


Fig. 3

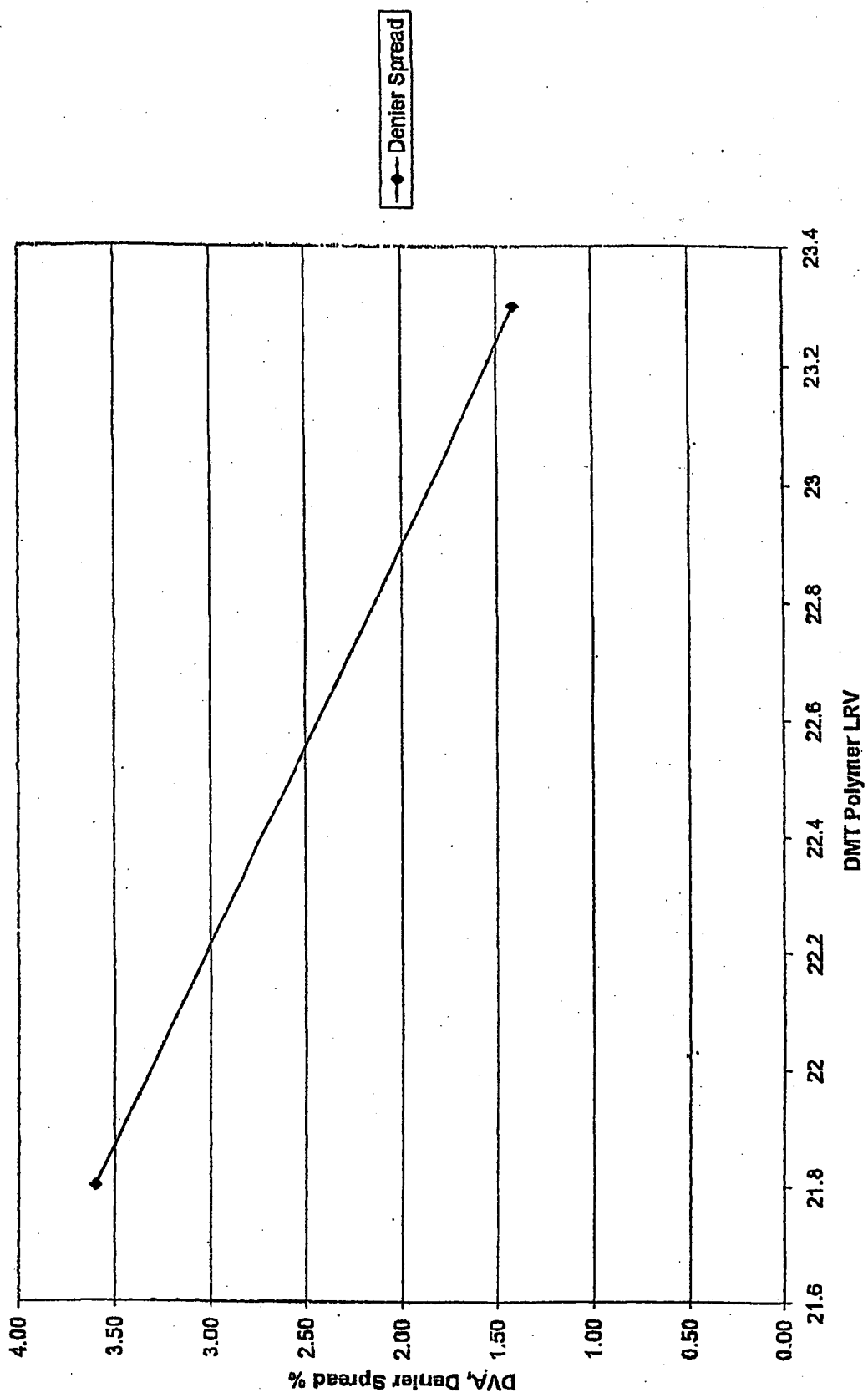


Fig. 4

INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/US 01/21545

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D01D5/092 D01F6/62 D01F6/84

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D01D D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 824 248 A (VASSILATOS GEORGE ET AL) 20 October 1998 (1998-10-20) cited in the application	1,2,4-6, 9,10, 12-15
Y	the whole document	3,7,8, 11,20
Y	EP 0 294 912 A (E.I. DU PONT DE NEMOURS AND COMPANY) 14 December 1988 (1988-12-14) the whole document	7,8,11, 20
P,Y	WO 00 63468 A (E.I. DU PONT DE NEMOURS AND COMPANY) 26 October 2000 (2000-10-26) the whole document	3
X	US 3 492 691 A (CARR PAUL LAMBTON INWOOD) 3 February 1970 (1970-02-03) claims; example 3	16-18
X	the whole document	19

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/21545

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5824248	A	20-10-1998	US 6090485 A	18-07-2000
EP 0294912	A	14-12-1988	BR 8800557 A	27-09-1988
			CN 88100818 A	05-10-1988
			EP 0294912 A2	14-12-1988
			FI 880605 A	12-08-1988
			IN 168956 A1	27-07-1991
			JP 1204925 A	17-08-1989
			JP 6021374 B	23-03-1994
			KR 9008723 B1	27-11-1990
			NO 880593 A	12-08-1988
WO 0063468	A	26-10-2000	WO 0063468 A1	26-10-2000
US 3492691	A	03-02-1970	GB 1088240 A	25-10-1967
			FR 1495029 A	18-12-1967
			NL 6611719 A	21-02-1967

1990-1991